5. (3)

AUTHORS: Mikhaylov, B. M., Ter-Gorkinyan, L. S., [illegible] SOV/62-[illegible]

TITLE: Polyene Compounds (Poliyenovyye soyedineniya). Communication 1. Synthesis of Arylpolyene Hydrocarbons by Means of Organometallic Compounds (Soobshcheniye 1. Sintez arilpoliyenovykh uglevodorodov pri pomoshchi metallorganicheskikh [illegible]

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, [illegible], pp. 1-9 (USSR)

ABSTRACT: In this work which is the continuation of previous communications (Refs 1, 2) syntheses between unsaturated aldehydes and ketones and organometallic compounds are investigated: benzyl sodium with the compounds benzyl aldehyde, cinnamic aldehyde, α-methyl cinnamic aldehyde, cinnamilidene acetone, and cinnamilidene acetophenone, and 1-[illegible]-phenylhexadiene-1,3-on-2. Special attention was given to the investigation of the synthesis of 1,3- and 1,4-aryl-substituted butadiene and hexatriene. Phenylbenzylether was synthesized according to the [illegible] (Ref 11). The experimental part shows a description of the synthesis of the individual substances. The [illegible]

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Polyene Compounds. Communication 4. Synthesis of [illegible]
Arylpolyene Hydrocarbons by Means of Organometallic Compounds

for the preparation of the individual compounds [illegible]
the synthesis benzyl sodium was attached to [illegible]
in 1,2-position and methylcinnamic [illegible]aldehyde a[illegible]
unsaturated ketone which has a methyl group in [illegible]
carbonyl group. The attachment of benzyl [illegible]
acetophone took place in the position [illegible]
ketone reacted with α-picolyl lithium in 1,2-position. [illegible]
lithium reacted with benzaldehyde or cinnamic[illegible]
with the formation of carbinols. In connection wit[illegible]
hydrogenation of the latter, isomers of the corresp[illegible]
hydrocarbons were formed. Moreover, new forms of polyene[illegible]
e.g. the compound (XVIII) were obtained. The following
compounds had been synthesized earlier: (VI) by Bower
(IX) by Koler (Ref 5), dimerization of butatriene
literature (Refs 6, 7), Whitby (Ref 8), (XIX) by [illegible].
There are 14 references, 7 of which are Soviet.

2 - final 2 pages

AUTHOR: Mikhaylov, B. M., Tovarov, L. A. SOV/62-59-5-13/40

TITLE: Polyene Compounds (Poliyenovyye soyedineniya). Communication 5. Synthesis of Asymmetrical Diarylpolyene Hydrocarbons ('Soobshcheniye 5. Sintez nesimmetrichnykh diarilpolyenovykh uglevodorodov)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, No 5, pp 910-912 (USSR)

ABSTRACT: In a previous paper the authors reported on the synthesis of arylated polyene hydrocarbons (Ref 1) which could be obtained by means of condensation products of benzaldehyde acetal with vinylethyl ether. Symmetrical polyenes of the type $C_6H_5(CH=CH)_nC_6H_5$ were obtained. In addition, a method for obtaining unsymmetrical polyenes was worked out. The unsymmetrical polyenes, already synthesized according to publications, are mentioned (Refs 2-3, 5, 7, 8). In this the synthesis of a number of phenyl-p-tolylpolyene hydrocarbons are described, which were obtained by condensation of ethoxyacetals with the magnesium derivatives of α-chloro-p-xylene by mixing the reagents, heating the

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Polyyne Compounds. Communication 5. Synthesis of Symmetrical Diarylpolyne Hydrocarbons SOV/62-59-5-12/40

[illegible] mixture and subsequent expulsion of ether at a temperature of 110-120°, and further dealcoholization of the intermediate product obtained by an aqueous alcoholic solution of [illegible] (Ref 14). The following substances were synthesized: 1,4-[illegible]-1-phenyl-4-p-tolylbutane; 1-phenyl-4-p-tolylbutadiene-1,3; 1,3,5-tri[illegible]-1-phenyl-6-p-tolylhexane; 1-phenyl-6-p-tolylhexatriene-1,3,5 and 1-phenyl-8-p-tolyloctatetraene-1,3,5,7. At first the phenyl-p-tolylpolyethoxyalkanes $C_6H_5-[CH(OC_2H_5)-CH_2]_{n+1}-C_6H_4-CH_3$ [illegible] were synthesized. After [illegible] aqueous alcoholic [illegible] solution, [illegible] of the general form $C_6H_5-(CH=CH)_{n+1}-C_6H_4-CH_3$ [illegible]. There are 3 references, [illegible]

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

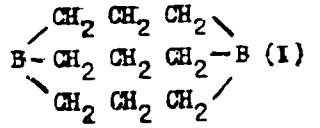
Card 2/2

5(3)
AUTHORS: Mikhaylov, B. M., Tutorskaya, F. B. SOV/62-59-6-29/36

TITLE: Derivatives of 1,5-Diborocycloöctane (Proizvodnyye 1,5-dibortsiklooktana)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 6, pp 1127 - 1130 (USSR)

ABSTRACT: In one of the author's earlier papers written in cooperation with Shchegoleva (Ref 1), he showed that the olefins with triisobutylboron form substituted borotrialkyls. In this connection the reaction of triisobutylboron and triallylboron was investigated. It is assumed that this reaction leads to the formation of a cyclic compound of the following composition:



(I)

In the reaction mentioned, polymers at first formed, which, by the action of alcohols, transformed into 1,5-dialkoxy-1,5-diborocycloöctane. The latter reacted with ethylamine under formation of 1,5-di(ethylamine)-1,5-diborocycloöctane. In the experimental part

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Derivatives of 1,5-Diborocycloöctane SOV/62-59-6-29/36

the production of the different substances is described in detail. All experiments were carried out in a nitrogen atmosphere. The physical constants of the different compounds produced are given. There are 3 Soviet references.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: December 1, 1958

Card 2/2

5 (3)

AUTHORS: Mikhaylov, B. M., Savel'yeva, I. S. SOV/62-59-7-21/38

TITLE: On the Influence of Thioacetic Acid on Aniles and Azobenzene (O deystvii tiouksusnoy kisloty na anily i azobenzol)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 7, pp 1304 - 1306 (USSR)

ABSTRACT: Mikhaylov and Blokhina (Refs 1,2) showed in a previous paper that polycyclic and aromatically substituted ethylene hydrocarbons enter into a conjugated reaction with thioacetic acid in the presence of oxygen under formation of dithioacetyl- or oxythioacetyl- hydrocarbon derivatives. The formation process of these compounds is investigated in the present paper in the case of the transformation of the azomethine compounds under the influence of thioacetic acid and in the presence of molecular oxygen. Benzophenone anile in thioacetic acid solution vehemently absorbs oxygen. The reaction mixture is heated and changes its color. The reaction is finished with the absorption of the equivalent quantity of oxygen. The authors obtained: acetanilide, benzophenone, diacetyl-disulphide, and sulphur. The reaction proceeds according to the following scheme:

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$(C_6H_5)_2C{=}NC_6H_5 + 3CH_3COSH + O_2 = C_6H_5NHCOCH_3 + (C_6H_5)_2CO +$
$+ (CH_3COS)_2 + S + H_2O$ (1). The effect of benzophenone anile in thioacetic acid in the case of lacking of oxygen was investigated in order to clarify the intermediate stages of the process. It was found that the intermediate compounds are acetanilide and thiobenzophenone (reaction scheme 2). The reaction process between acetophenone anile and thioacetic acid is analogous. The mentioned change in color (during the reaction, into blue) proves the formation of thiobenzophenone as intermediate product. Diacetyl-disulphide, sulphide, and hydrogen sulphide are produced from thioacetic acid during the reaction. N-acetyl-hydrazobenzene is formed in the case of heating of azobenzene with the threefold equivalent of thioacetic acid according to the following scheme: $C_6H_5N{=}NC_6H_5 + 3\,CH_3COSH =$

$= C_6H_5NH\text{-}\underset{\underset{COCH_3}{|}}{N}C_6H_5 + (CH_3COS)_2 + H_2S$ (4).

On the Influence of Thioacetic Acid on Aniles and Azobenzene SOV/62-59-7-21/38

The reactions are described in detail in the experimental part. There are 7 references, 2 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: November 11, 1957

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5(3)

AUTHORS: Mikhaylov, B. M., Shchegoleva, T. A. SOV/62-59-8-8/42

TITLE: Boron-organic Compounds. Communication 42. Alkylpyro-boroacetic Anhydrides

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 8, pp 1393-1396 (USSR)

ABSTRACT: It was shown in the present paper that the mixed anhydrides of fatty acids and n-propylpyro boric acid normally formed under the influence of organic acids upon esters of n-propylchloro boric acid may be obtained much more easily by heating alkyl boric acid with the anhydride of acetic acid over a water bath. In this way it was possible to synthesize the anhydrides of n-propylpyro-boroacetic acid (I), isopropylpyro-boroacetic acid (II), and n-butylpyro-boroacetic acid (III) as well as isobutylpyro-boroacetic acid (IV), with yields ranging between 60 and 70% of the theoretical yields. The compounds obtained were investigated as to their different reactivities. It was shown that the anhydrides of alkylpyro-boroacetic acid easily react with the esters of alkyl boric acid at 160-185°, forming the anhydrides of alkyl boric acid. The anhydride of n-propylpyro boric acid forms a mixture of

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Boron-organic Compounds. Communication 42: Alkylpyro- SOV/62-59-8-8/42
boroacetic Anhydrides

anhydrides of propyl and phenyl boric acids when heated with the esters of phenyl boric acid. The anhydride of n-propyl-pyro boric acid forms anhydride of propyl boric acid also with the esters of n-propylchloro boric acid. In the experimental part the reaction method is described. There is 1 Soviet reference.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: November 21, 1957

Card 2/2

5(3) SOV/62-59-8-24/42

AUTHORS: Mikhaylov, B. M., Fedotov, N. S.

TITLE: Complex Compounds of Diphenyl Boron Chloride With Primary Amines and N-Substituted Derivatives of Diphenylamino Boron

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 8, pp 1482-1483 (USSR)

ABSTRACT: The present paper is a continuation of investigations made concerning the reaction of diarylborochloride and amines (Ref 1). The primary amines form, in contrast with the secondary amines, complexes with the above compounds where two amino molecules are to be found for each chloride molecule:

$(C_6H_5)_2BCl + 2RNH_2 = (R_6H_5)_2BCl.2RNH_2$

R being CH_3-, C_2H_5-, $i\text{-}C_4H_9$

So far, these compounds had been unknown. Similar compounds (alkylboron difluorides with two alcohol molecules) had been obtained by Mikhaylov and Shchegoleva (Ref 3). The structure of the molecules obtained here is considered either a hydrogen-bond structure (II) or heteropolar (III). The saline character and the low volatility suggest (III). When the temperature is raised

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Complex Compounds of Diphenyl Boron Chloride With Primary Amines and N-Substituted Derivatives of Diphenylamino Boron

SOV/62-59-8-24/42

above the melting point, the molecule decomposes and forms N-substituted diphenylamino boron (IV) and alkylamino chloride. Compound (I)(R = CH_3) changes when left undisturbed into the crystalline dimer which is probably of a cyclic structure (V). The existence of the complexes investigated and their thermal transformation throw some light upon the reaction mechanism of the substitution for the chlorine atoms at the amino group in boron-organic halogenides. The experimental part describes in detail the individual transformation reactions. There are 3 references, 2 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: December 17, 1958

Card 2/2

SOV/51-6-3-12/28

AUTHORS: Nikitina, A.N., Galanin, M.D., Ter-Sarkisyan, G.S. and Mikhaylov, B.M.

TITLE: The Absorption and Luminescence Spectra of Solutions of Substituted Polyenes (Spektry pogloshcheniya i lyuminestsentsiya rastvorov nekotorykh zameshchennykh poliyenov)

PERIODICAL: Optika i Spektroskopiya, 1959, Vol 6, Nr 3, pp 354-360, (USSR)

ABSTRACT: The authors investigated the electronic absorption spectra of eighteen substituted butadienes and hexatrienes dissolved in heptane as well as luminescence of solutions of these substances in heptane and benzene. All the substances studied were purified chromatographically using aluminium oxide. The absorption spectra of solutions were measured using a spectrophotometer SF-4. The luminescence spectra in the visible region were measured by means of a spectrometer consisting of a monochromator UM-2 and a photomultiplier FEU-19. The results obtained are shown in Table 1. This table includes calculated values of the oscillator

Card 1/2 strengths of long-wavelength electronic transitions and the

The Absorption and Luminescence Spectra of Solutions of Substituted Polyenes

quantum yields of luminescence. The absorption spectra of solutions of the substituted butadienes and hexatrienes are shown in Figs.1-8. It was found that the absorption intensities and band positions depend on the degree of departure from coplanarity of conjugated double bonds. It was found also that the quantum yield of luminescence of some substances is higher in benzene solutions and in others it is higher in heptane solutions. Measurements of the excited-state lifetime showed that decrease of the quantum yield of 1,1,4,4-tetraphenyl-butadiene-1,3 in a benzene solution is due primarily to quenching of the second type, while changes of the excited-state lifetime of 1,6-diphenyl-hexatriene-1,3,5 cannot be explained by quenching (Table 2). There are 8 figures, 2 tables and 11 references, of which 2 are Soviet, 8 English and 1 German.

SUBMITTED: January 16, 1958

5 (3)

AUTHOR: Mikhaylov, B. M.

TITLE: Organic Compounds of Boron

PERIODICAL: Uspekhi khimii, 1959, Vol 28, Nr 12, pp 1459-1487 (USSR)

ABSTRACT: In this survey, work in the field of organoboron compounds published from 1956 to 1958, and, in part, also in 1959 is summarized. Work on the investigations performed on boron compounds without boron-carbon bond, such as boric acid esters, its amides etc. is included. Investigations related to this topic were, for the major part, discussed in a recently published paper (Ref 2) on the reaction of boron chloride with organic compounds. In this paper, methods of preparation for boron trialkyls (Refs 1, 3, 4 to 39), boron triaryls (Refs 1, 42 to 46) as well as their properties (Refs 47-52, 13, 28) are described. The physical properties of symmetric R3B type compounds are given in table 1, of asymmetric ones in tables 2 and 3. The second part of this paper is devoted to the oxygen derivatives of organoboron compounds involving monosubstituted organoboric acids and their derivatives (Refs 1, 28, 53 to 54). The physical properties of some monosubstituted organoboric acids recovered are summarized in table 4, of their anhydrides

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in table 5, and of their esters in table 6. Moreover, disubstituted organoboric acids and their derivatives are treated. Methods of preparation used for disubstituted organoboric acid esters (Refs 16, 28, 44, 54, 55, 97, 105-118), their properties (Refs 87, 108 to 110, 119 to 122), methods of preparation and properties of disubstituted organoboric acids and their anhydrides (Refs 16, 40, 41, 44, 86, 108 to 110, 123 to 126) are described. The physical properties of disubstituted organoboric acids are summarized in table 7, of their anhydrides in table 8, of the esters of symmetric acids in table 9, and of the esters of asymmetric acids in table 10. The third section deals with the haloderivatives of organoboron compounds. Methods of preparation used for haloderivatives of organoboric acids (Refs 1, 28, 37, 41, 47, 68, 96, 98, 99. 101, 102, 110, 112, 116, 119, 120, 127, 129 to 143) as well as their properties (Refs 14, 74, 95, 101, 110, 112, 134, 137, 139 to 141, 144 to 146) are described. The physical properties of different types of haloderivatives of organoboron compounds are given in tables 11 to 14. In the fourth section, the thioderivatives of organoboron compounds are briefly discussed (Refs 1, 16, 148 to 151). Properties of the

esters of organic thioboric acids are given in tables 15 and 16. In the fifth section of the paper, the nitrogen derivatives of organoboron compounds, i.e. borazoles (Refs 1, 16, 28, 100, 102, 132, 147 to 149), are treated by the author. Physical properties of $R_2BHR'_2$ type organoboron compounds are given in table 17, of $RB(NR'_2)_2$ type organoboron compounds in table 18, of the amino esters of $RB<^{OR'}_{NR''}$ type organoboric acids in table 19, and of tri- and hexasubstituted borazole derivatives in table 20. The lively interest in organoboron compounds is attributed to both their theoretical importance for organic chemistry and to their practical possibilities for application. For their high heating power, boron hydrides and organoboron compounds are high-grade propellants for jet engines. Polyboronorganosiloxanes and boron-containing organic polymers can be obtained from organoboron compounds. Organoboron compounds are being used in fluid scintillators to record neutrons (Ref 175). They can be of importance to biology and medicine also (Refs 89, 176). The author repeatedly refers to his own papers, and cites the

Organic Compounds of Boron SOV/74-[illegible] - 7/25

names of the following Soviet scientists: T. A. Shcherboleva, L. I. Zakharkin, O. Yu. Okhlobystin, V. A. Vaver, P. L. Aronovich, N. S. Fedotov, Yu. N. Bubnov, A. F. Zhigach, L. N. Kochneva. There are 20 tables and 176 references, 60 of which are Soviet.

ASSOCIATION: In-t organicheskoy khimii im. N. D. Zelinskogo AN SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy, AS USSR)

Card 4/4

AUTHORS: Mikhaylov, B. M., Chernova, N. G. SOV/79-29-1-47/74

TITLE: On Dioxane- and Dioxane Benzene Complexes of the Lithium-Aromatic Compounds (O dioksanovykh i dioksanovo-benzol'nykh kompleksakh litiyaromaticheskikh soyedineniy)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 1, pp 222 - 228 (USSR)

ABSTRACT: The authors synthesized the complex compounds of lithium aryls with dioxane (Ref 1) to begin with by mixing the benzene solution of n.-butyl lithium with the dioxane solutions of aryl bromide according to the scheme $ArBr+n.\text{-}C_4H_9Li \rightarrow ArLi+n.\text{-}C_4H_9Br$. The share of dioxane in the compounds thus obtained was calculated by determining their metal content and in the case of derivatives of the solid hydrocarbons by determining the hydrogen share. In the case of investigation of the dioxane complex of 3-pyrenyl lithium (Ref 2) not only the metal and the hydrocarbon content were determined but also the dioxane itself. In this connection it was found that this complex contains also another product apart from dioxane. Basing upon this

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observation also the earlier obtained complex compounds of lithium aryls were quantitatively investigated with respect to dioxane in which connection it was found that in some of them the amount of lithium aryl and dioxane amounted to 72-86% of the complex weight. Thus, the conclusion was drawn that benzene which was used as solvent forms also part of the complex (Ref 2). Tables 1 and 2 may serve as illustrations of this case. Summarizing, the following investigation results are to be mentioned: In the case of action of benzene solution of n-butyl lithium upon aryl bromides in the presence of dioxane, dioxane-benzene complexes of the lithium-aromatic compounds of the composition $2ArLi.2C_4H_8O_2.C_6H_6$ are formed. These complexes form phenyl lithium, p-tolyl lithium, o-tolyl lithium. p-chlorophenyl lithium and 3-pyrenyl lithium. 9-phenanthryl lithium and 9-anthryl lithium form correspondingly the complexes $ArLi.C_4H_8O_2$ and $ArLi.2C_4H_8O_2$. In the case of action of the hexane solution of n.-butyl lithium upon the aryl bromides in the presence of dioxane

the complexes 2 $ArLi.3C_4H_8O_2$ or $ArLi.2C_4H_8O_2$ are obtained. Thus the nature of the solvent exercises an influence upon the composition of the dioxane complexes of the lithium-aromatic compounds. There are 3 tables and 13 references, 8 of which are Soviet.

ASSOCIATION: Institut eksperimental'noy patologii i terapii raka (Institute of Experimental Cancer Pathology and Therapy)

SUBMITTED: November 5, 1957

5(3) SOV/79-29-4-48/77

AUTHORS: Mikhaylov, B. M., Aronovich, P. M.

TITLE: Organo-boron Compounds (Bororganicheskiye soyedineniya). XXXIV. Alkylphenylboron Chlorides (Alkilfenilborkhloridy)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 4, pp 1254-1257 (USSR)

ABSTRACT: The authors continued their work in the field of the synthesis of organo-boron compounds of the fatty aromatic series (Ref 1) and synthesized, during the work discussed in this article, the isobutyl ester of ethylphenyl boric acid (II) by transformation of lithium ethylate with phenyl boric acid:

$$C_6H_5B(OC_4H_9)_2 + C_2H_5Li \rightarrow \left[\begin{matrix} C_6H_5 \\ C_2H_5 \end{matrix}\right]B(OC_4H_9)_2\,Li \rightarrow$$

(I)

$$\begin{matrix} C_6H_5 \\ C_2H_5 \end{matrix}\Big\rangle BOC_4H_9 \quad (II)$$

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Organo-boron Compounds. XXXIV. Alkylphenylboron Chlorides

It was shown that the ethylphenyl di-isobutoxyboreniate of lithium (I), which forms in the first stage, decomposes not only with HCl but also with diluted hydrochloric acid. Such a simplification is also possible in the synthesis of the esters of n-propylphenyl- and n-butylphenyl boric acid, since the lithiumalkylphenyl di-isobutoxyboreniates, in contrast with the diphenyl di-isobutoxyboreniates of lithium (Ref 3), decompose in one direction only with diluted hydrochloric acid, while the esters of alkylphenyl boric acids are formed simultaneously. The isobutyl esters of alkylphenyl boric acids are equally stable in the hydrolysis as the alkyl esters of dialkyl- and diaryl boric acids (Refs 4,5,6). By reaction with PCl_5 the alkylphenylborates change into alkylphenyl boron chlorides (76-83% yield). The reaction follows the scheme:

$$\begin{matrix} R \\ C_6H_5 \end{matrix}\!\!>\!BOC_4H_9 + PCl_5 \rightarrow \begin{matrix} R \\ C_6H_5 \end{matrix}\!\!>\!BCl + POCl_3 + \text{iso-}C_4H_9Cl$$

Organo-boron Compounds. XXXIV. Alkylphenylboron Chlorides

In this way the methylphenyl-, ethylphenyl-, n-propylphenyl-, and n-butylphenyl boron chlorides were prepared. There are 1 table and 8 references, 6 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences USSR)

SUBMITTED: February 24, 1958

SOV/79-29-4-49/77

5(3)
AUTHORS: Mikhaylov, B. M., Aronovich, P. M.

TITLE: Organo-boron Compounds (Bororganicheskiye soyedineniya). XXXV. Alkylphenyl Boric Acids and Their Anhydrides (XXXV. Alkilfenilbornyye kisloty i ikh angidridy)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 4, pp 1257-1262 (USSR)

ABSTRACT: With the exception of a paper published by K. Torssell (Ref 1), in which the reaction conditions and constants of the synthesized product were not given, alkylphenyl boric acids have so far not been described. As has been reported (Ref 2), the authors did not succeed in realizing the hydrolysis of the isobutyl esters of alkylphenyl boric acids. During a further attempt to obtain alkylphenyl boric acids through the influence of water on alkylphenyl boron chlorides (Ref 2) it was found that the nature of the alkyl radical exerts a great influence on the behavior of these chlorides with respect to water. When reacting with water ethylphenyl boron chloride does not form, as expected, ethylphenyl boric acid but only ethyl boric acid. Among the further negative cases only n-butylphenyl

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Organo-boron Compounds. XXXV. Alkylphenyl Boric Acids and Their Anhydrides

boron chloride reacts normally with water, and the corresponding acid is formed. The hydrolysis mechanism of alkylphenyl boron chlorides is apparently connected with the processes of a complex formation, as usually observed in boron compounds [Schemes (1). (2), and (3)]. Compound (I) first affiliates the water molecule and forms the complex compound (II) which splits off HCl and thus changes into (III). In this process (II) splits off benzene, and (IV) is formed. These results of the hydrolysis with water show that benzene can only be prevented from being split off by binding the hydrogen chloride removed in the course of the reaction. Indeed, it was possible to obtain the alkylphenyl boric acids by saponification of the chlorides with an equimolecular amount of alkali lye. When distilled, the methyl-, ethyl-, and n-propylphenyl boric acids split off water and form anhydrides. In this process n-butylphenyl boric acid disproportionates. Thus, by the hydrolysis of alkylphenyl boron chlorides with water a mixture of alkylphenyl- and alkyl boric acid is formed. There are 2 tables and 5 references, 3 of which are Soviet.

SOV/79-29-4-49/77

Organo-boron Compounds. XXXV. Alkylphenyl Boric Acids and Their Anhydrides

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences USSR)

SUBMITTED: February 24, 1958

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5(3)

AUTHORS: Mikhaylov, B. M., Kostroma, T. V. SOV/79-29-5-15/75

TITLE: Organoboron Compounds (Bororganicheskiye soyedineniya). 36. Synthesis of Hexasubstituted Compounds of "Borazol" From Esters of the Aryl-chloroboric Acid (36. Sintez geksazameshchennykh borazola iz efirov arilkhlorbornykh kislot)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 5, pp 1477-1483 (USSR)

ABSTRACT: In order to devise a method of synthesizing "borazol" derivatives in the present paper thermal transformations of some esters of aryl-ethyl-amino-boric acids as well as of aryl-phenyl-amino-boric acids were investigated. By the influence of ethyl amine upon esters of the aryl-chloroboric acid isobutyl esters of the p-toluene-ethyl-amino-boric, o-toluene-ethyl-amino-boric and α-naphthyl-ethyl-amino-boric acid were obtained. The opinion expressed in reference 1 regarding the transformation mechanism of the esters of the aryl-ethyl-amino-boric acid into "borazol" compounds and esters of the aryl-boric acid was revised. It was concluded that "borazol" compounds are formed by separation of alcohol directly from amino esters (I). Further the alcohol reacts with the initial amino ester thus forming the ester of aryl-boric acid and ethyl-amine. Owing to this reaction one half of the ester of the aryl-ethyl-amino-boric

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acid must be converted into the "borazol" compound and the other into the ester of the aryl-boric acid which really took place. This reaction mechanism was confirmed by the ready transformation of aryl-bis-(ethylamino)boron (II) into B-triaryl-N-triethyl-borazol, which took place in the presence of small alcohol quantities. The experiment indicated that phenyl-bis-(ethylamino)-boron is transformed into B-triphenyl-N-triethyl-borazol on heating up to 260° in the presence of small amounts of butyl alcohol. The yield is 85%. Without alcohol its yield is only 17% (Ref 2). With aniline the esters of the aryl-chloro-boric acid yield the aniline hydrochloride and esters of aryl-phenyl-aminoboric acid which can, however, not be prepared in a pure form. During distillation in vacuum at 15-20 mm they are cleaved to give aniline, esters of the aryl-boric acid and B-triaryl-N-triphenyl-borazols. In this way the hexaphenyl-borazol was obtained from the ester of the phenyl-boric acid (30%) and the B-tri-p-tolyl-N-triphenyl borazol (39.4%) from the ester of the p-toluyl-chloroboric acid and aniline. The formation mechanism of borazol compounds from esters of the aryl-phenyl-aminoboric acid differs from the mechanism of the thermal transformation of esters

Organoboron Compounds.
36. Synthesis of Hexasubstituted Compounds of "Borazol" From Esters of the Aryl-chloroboric Acid

of the aryl-ethyl-aminoboric acid. In contrast with the latter they are cleaved at about 200° symmetrically into esters of the aryl-boric acid and aryl-bis(phenylamino)boron (VI) which are transformed at 300-400°, after separation of aniline, to give hexaaryl-borazols. In this way the phenyl-bis(phenylamino)boron (79.4%) was obtained from esters of the phenyl-phenylamino-boric acid and the p-tolyl-bis(phenylamino)boron (83.6%) from the esters of the p-tolyl-phenyl-aminoboric acid. In accordance with the mechanism mentioned "borazol" compounds are formed from amino esters (V) in the same yield (about 30%) as on thermal decomposition of aryl-bis(phenylamino-) boron. The phenyl-bis-(phenylamino-)boron is converted in the presence of small amounts of butyl alcohol into hexaphenyl-borazols in the same yield as without alcohols. All "borazol" derivatives obtained possess a stability unusual for organoboron compounds with respect to atmospheric oxygen and moisture. There are 2 Soviet references.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR

Organoboron Compounds. SOV/79-29-5-15/75
36. Synthesis of Hexasubstituted Compounds of "Borazol" From Esters of the Aryl-chloroboric Acid

(Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: February 24, 1958

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5(3) S V/79-29-5-16/75

AUTHORS: Mikhaylov, B. M., Blokhina, A. N., Kostroma, T. V.

TITLE: Organoboron Compounds (Bororganicheskiye soyedineniya). 37. Synthesis of B-Triarylborazols From Aryl Boron Dichlorides (37. Sintez B-triarilborazolov iz arilbordikhloridov)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 5, pp 1483 - 1486 (USSR)

ABSTRACT: Reference 1 describes the reaction of phenylboron-dichloride with ammonia, where B-triphenyl borazol is formed. In the present paper it was found that also other aryl-boron dichlorides react with ammonia in a similar way. The samples required for the investigation were prepared by means of reaction of arylboric acid esters with phosphorus pentachloride, p-chlorophenyl-boron dichloride and p-bromo-phenyl-boron-dichloride. On introduction of ammonia into benzene solution of aryl-boron-dichloride its ammoniate is formed at room temperature. On heating its benzene suspension in the water bath and on continued introduction of ammonia the ammoniate is tranformed into ammonium chloride and B-triaryl-borazol. In this way B-tri-p-tolyl-borazol, B-tri-p-chlorophenyl-borazol and B-tri-p-bromo-

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Organoboron Compounds. 37. Synthesis of B-Triarylborazols S/ V/79-29-5-1../75
From Aryl Boron Dichlorides

phenyl-borazol were obtained in yields of 65 - 91%. The reaction mechanism probably consists of a transformation of the aryl-boron dichloride initially formed (I) into aryl-chloro-amino-boron (II). The molecules of the latter condense with one another and form triaryl-borazol. The B-triaryl-borazols are extremely stable with respect to atmospheric moisture and oxygen as compared with other organoboron compounds. The phenyl-boron-dichloride yields complex compounds with triethyl-amine. There are 3 references, 2 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: February 24, 1958

Card 2/2

5(3)

AUTHORS: Mikhaylov, B. M., Ter-Sarkisyan, G. S. SOV/79-29-5-50/75

TITLE: Polyene Compounds (Poliyenovyye soyedineniya). VII. Condensation of Vinyl-Ethyl-Ether With the Acetals of Aromatic Aldehydes and Ketones (Kondensatsiya viniletilovogo efira s astetalyami aromaticheskikh al'degidov i ketonov)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 5, pp 1642-1648 (USSR)

ABSTRACT: As a first example in the series of aliphatic-aromatic ketones the authors investigated the reaction between diethyl ketal of acetophenone and the vinyl-ethyl-ether. This reaction is much more complicated than the one between acetals of aromatic aldehydes and α,β-unsaturated ethers. The following was isolated from the mixture: 3-phenyl-1,1,3-triethoxy butane, 5-phenyl-1,1,5-triethoxy hexene-2, 7-phenyl-1,1,7-triethoxy octadiene-2,4, 9-phenyl-1,1,9-triethoxy-decatriene-2,4,6 and diethyl acetal of acetal aldehyde. The structure of 3-phenyl-1,1,3-triethoxy butane was proven by saponification with diluted hydrochloric acid to 3-phenyl-3-ethoxy-butanal-1 and,, under heavier conditions, to β-methyl cinnamaldehyde.

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Polyene Compounds. VII. Condensation of Vinyl-Ethyl- Ether With the Acetals of Aromatic Aldehydes and Ketones SOV/79-29-5-50/75

In order to determine the position of the ethoxy group in 5-phenyl-1,1,5-triethoxy hexene-2, the diethyl acetal of β-methyl cinnamaldehyde was entered into reaction with vinyl ethyl ether and 5-phenyl-1,1,3-triethoxy hexene-4 was obtained therefrom. Both hexene derivatives (hexene-2, hexene-4) were hydrolyzed and the aldehyde obtained was identified by its 2,4-dinitrophenyl hydrazone. Moreover, hexene-2-derivative was obtained by direct synthesis from acetophenone acetal and 1-ethoxy butadiene-1,3. Both higher condensation products were not investigated more closely. The experimental describes the reactions carried out and gives the physical and analytical data of the initial substances as well as of the compounds obtained. There are 8 references, 1 of which is Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences of the USSR)

SUBMITTED: April 15, 1958

Card 2/2

5(3)
AUTHORS: Mikhaylov, B. M., Bubnov, Yu. N. SOV/79-29-5-51/75

TITLE: Boron Organic Compounds (Bororganicheskiye soyedineniya). XXXVIII. The Reaction of Boron Trialkyls With Sulphur. Synthesis of Esters of the Dialkyl-Thio-Boric Acids (XXXVIII. Reaktsiya bortrialkilov s seroy. Sintez efirov dialkiltiotornykh kislot)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 5, pp 1648-1650 (USSR)

ABSTRACT: The authors investigated the problem, to what extent there is a parallel between the reaction of boron trialkyls with sulphur and with oxygen. Experiments showed that tri-n.-propyl boron and tri-n-butyl boron with sulphur on heating up to 145° supply the corresponding di-esters of thioboric acid: $R_3B + S \longrightarrow R_2BSR$. In analogy with the reaction with oxygen trialkyl boron probably forms first a molecular compound with sulphur, which then enters reaction with a second molecule of trialkyl boron: $R_3B + S_n = R_3B \leftarrow S_n$; $R_3B \leftarrow S_n + R_3B = 2R_2BSR + S_{n-2}$ Publications hitherto

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revealed only the methyl ester of dimethyl thioboric acid, which however was obtained from the reaction between methyl mercaptan and tetramethyl diborane or dimethyl boron bromide (Refs 2,3). Esters of dialkyl thioboric acids are uneffected by temperature changes and very reactive. In water they hydrolyze to dialkyl boric acids; under the effect of alcohols they form esters of dialkyl boric acids. Thus, methyl ester of di-n.propyl boric acid was obtained from the n.-propyl ester of di-n.-propyl thioboric acid and methyl alcohol. Esters of dialkyl thioboric acids react with amines under formation of dialkyl boramine substituted at the nitrogen. In this way, the authors obtained di-n.-propyl isobutyl amino boron and di-n.-butyl phenyl amino boron. The experimental contains the exact description of the reactions mentioned as well as the analytical and physical data of the substances obtained. There are 3 references.

Boron Organic Compounds. XXXVIII. The Reaction of Boron Trialkyls With Sulphur. Synthesis of Esters of the Dialkyl-Thio-Boric Acids

SOV/79-29-5-51/75

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences of the USSR)

SUBMITTED: April 9, 1958

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5 (3)

AUTHORS: Mikhaylov, B. M., Povarov, L. S. SOV/79-29-6-66/72

TITLE: Polyene-Compounds (Poliyenovyye soyedineniya). VIII. Reactions of Some Acetals With Unsaturated Ethers (VIII. Reaktsii nekotorykh atsetaley s nepredel'nymi efirami)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 6, pp 2079 - 2083 (USSR)

ABSTRACT: It was recently discovered, that acetals can react with ethers, which have conjugated double bonds, and form products, which are bound to the diene in position 1,4 (Refs 1-6). These reactions have been used in the present study for the synthesis of some derivatives of aldehydes of the terpene series. It was proved, that citral acetal (I) reacts smoothly in presence of zinc (II) chloride with the compound (II), forming acetal (III) and acetal (IV) according to scheme 1. The compound (III) is a derivative of farnesol, and (IV) a derivative of di-terpene aldehyde. The reaction of the α, β-unsaturated ethers with acetals was used for the synthesis of acetal (VIII). The acetal (VI) has been condensed in presence of zinc (II) chloride with (V), forming (VII). This compound has been converted by condensation with vinyl ethyl ether into acetal of the 3,5 di-ethoxy-

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3,7-di-methyloctane-6-ol-7 (VIII). This final product is the acetal of di-ethoxy citronellal (scheme 2). The authors obtained the initial product (II) by the effect of catalytic quantities of the n-toluol sulphonic acid in quinoline upon butane (IX). This method could also be used for the synthesis of the 1-ethoxy butadiene-1,3 from 1,1,3-tri-ethoxy butane. The compounds (X) and (XI) were obtained by condensation of the compound (IX) with vinyl ethyl ether (scheme 3). There are 7 references, 5 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: July 22, 1958

5 (3)
AUTHORS: Mikhaylov, B. M., Fedotov, N. S. SOV/79-29-7-30/93

TITLE: Organoboron Compounds (Bororganicheskiye soyedineniya). XXXVI. Asymmetrical Diaryl Boric Acids and Their Derivatives (XXXVI. Nesimmetrichnyye diarilbornyye kisloty i ikh proizvodnyye)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 7, pp 2244 - 2248 (USSR)

ABSTRACT: One part of the diaryl boric acids form complex compounds with water of the type $Ar_2B(OH)(OH_2)$ (A), the other part contains no water, it has, however, the effect of Lewis acids in aqueous solutions, i.e. with bases they form the same salts (B) as the acids of the hydrate form (A). The authors continued their investigation of the complex formation in the series of aromatic boron compounds and synthesized some unsymmetrical diaryl boric acids, their esters, and acid chlorides, and investigated their capability of complex formation. The isobutyl esters of unsymmetrical diaryl boric acids (V) were synthesized by the reaction of the corresponding Grignard reagents with the isobutyl

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ester of phenyl boric acid (Scheme 1). In this case the isobutyl esters of phenyl-p-tolyl-, phenyl-p-bromophenyl-, and phenyl-α-naphthyl boric acid were obtained. These esters form stable complex compounds (C) with ammonia. The isobutyl esters of phenyl-p-tolyl- and phenyl-α-naphthyl boric acid were transformed with PCl_5 into the chlorides, phenyl-p-tolyl boron chloride and phenyl-α-naphthyl boron chloride (Scheme 2). The diaryl boron chlorides form the following solid complex compounds with dioxane (1:1): phenyl-p-tolyl boron chloride-, phenyl-α-naphthyl boron chloride- as well as diphenyl boron chloride and di-α-naphthyl boron chloride dioxanate (Ref 4) (Scheme 3), which were synthesized already earlier. In the hydrolysis of the phenyl-α-naphthyl- and phenyl-p-tolyl boron chloride, the phenyl-α-naphthyl- and phenyl-p-tolyl boric acid are formed which contain no complex water (Scheme 4). The latter acid is extremely unstable and decomposes according to scheme 5. There are 5 Soviet references.

Organoboron Compounds. XXXVI. Asymmetrical Diaryl Boric Acids and Their Derivatives SOV/79-29-7-30/83

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: June 18, 1958

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5 (3)
AUTHORS: Mikhaylov, B. M., Vaver, V. A. SOV/79-29-1-31/85

TITLE: Organoboron Compounds (Bororganicheskiye soyedineniya). XXXVII. Lithium Salts of the Diaryl Boric Acids and Their Complex Compounds with Dioxane (XXXVII. Litiyevyye soli diarilbornykh kislot i ikh kompleksnyye soyedineniya s dioksanom)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 1, pp 224B-2253 (USSR)

ABSTRACT: In continuation of earlier investigations the authors show that diaryl boric acids react like protonic acids in annydrous media. Unexpectedly they obtained the lithium salt of di-α-naphthyl boric acid $(\alpha\text{-}C_{10}H_7)_2BOLi$ (I) as the main product in the reaction of phenyl lithium with di-α-naphthyl boric acid. This salt is formed even more easily from n.-butyl lithium and di-α-naphthyl boric acid in benzene solution (Scheme 2). The reaction of n.-butyl lithium with di-o-tolyl boric acid (Scheme 3), which leads to the formation of a mixture from the lithium salts of di-o-tolyl- and o-tolyl butyl boric acid, is much more complicated. Their formation is explained by the decomposition of compound (III), in contrast to (II), under the separation of butane and toluene. With dioxane in absolutely anhydrous ether

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Organoboron Compounds. XXXVII. Lithium Salts of SOV/79-29-1-51/83
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it was possible to separate from this salt mixture the pure lithium salt of the di-o-tolyl boric acid in the form of its complex compound with dioxane. The lithium salt of o-tolyl-butyl boric acid could not be separated, its presence, however, was found to be probably due to the resultant per cent content of boron (Refs 4,5). In order to prevent the formation of salts of aryl butyl boric acids, only o-tolyl or p-tolyl lithium were used in the experiments for obtaining the lithium salts of di-o-tolyl- and di-p-tolyl boric acid. The necessary individual organolithium compounds were obtained by the reaction of n.-butyl lithium with aryl bromides in benzene dioxane solution and in the form of their crystalline dioxanates (Ref 6). The p-tolyl lithium was synthesized from n.-butyl lithium and tri-p-tolyl antimony (Ref 6). By this method the lithium salt of di-p-tolyl boric acid and the dioxanate of the lithium salt of the di-o-tolyl boric acid were obtained. The dioxanates of the lithium salts of the diaryl boric acids may be synthesized directly by the reaction of lithium compounds with the dioxanates of the diaryl boric acids (e. g. compound (V) according to

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Organoboron Compounds. XXXVII. Lithium Salts of the Diaryl Boric Acids and Their Complex Compounds With Dioxane SOV/79-29-7-31/83

scheme 5). There are 7 references, 6 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: June 26, 1958

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5(3) SOV/79-29-8-22/81

AUTHORS: Mikhaylov, B. M., Ter-Sarkisyan, G. S.

TITLE: Polyene Compounds. IX. Condensation of Acetals of Furyl-, Cinnamic- and Furyl-acrylic Aldehyde With Unsaturated Ethers

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 8, pp 2560-2565 (USSR)

ABSTRACT: In addition to previous papers (Refs 1,2), the present paper deals with the condensation of the diethyl acetals of the above-mentioned aldehydes with the vinyl ethyl ether and 1-ethoxy-butadiene-1,3. The reaction of these diethyl acetals with α,β-unsaturated ethers takes place readily in the presence of the acetic acid solution of zinc chloride, and yields the corresponding ethoxy derivatives of the aromatic and furane series which by boiling with acetic acid (Ref 3), are easily transformed into the unsaturated aldehydes. The reactions of the diethyl acetals of the above-mentioned aldehydes with vinyl ethyl ether gave, in fair yields, the condensation products of acetal, mostly with one molecule of vinyl ethyl ether already at equimolar ratios of the reagents. Thus, the diethyl acetal of the cinnamic aldehyde reacts with this ether under formation of

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Polyene Compounds. IX. Condensation of Acetals of Furyl-, Cinnamic- and Furyl-acrylic Aldehyde With Unsaturated Ethers

compound (I) which is transformed, by boiling with glacial acetic acid, to give (II) in good yield. This method is of preparative importance, and better than the previous condensation according to reference 4 (Scheme 1). Compound (III) can be obtained as easily, which is transformed by boiling with acetic acid into the acrolein (IV) which had formerly been synthesized from furfurole and acetic anhydride (Ref 5) (Scheme 2). The reaction of compound (V) with vinyl ethyl ether gives (VI), and further, with acetic acid, pentadienal (VII) (Scheme 3). On reaction of the double quantity of diethyl acetal of the cinnamic aldehyde with 1-ethoxy-butadiene-1,3, compound (VIII) resulted which further gives compound (IX) by boiling with acetic acid (Scheme 4). Further compounds of this kind (X)-(XIII) were synthesized for the first time (Schemes 5,6,7). There are 7 references, 2 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences, USSR)

SOV/79-29-9-67/76

5(3)

AUTHORS: Mikhaylov, B. M., Aronovich, P. M.

TITLE: Organoboron Compounds. XLV. Reaction of Butyl Esters of Boric Acid and Boronorganic Acids With Aromatic Amines

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 9, pp 3124-3129 (USSR)

ABSTRACT: The present investigation was made to explain the capability of alkoxy groups of the esters of boric acid and their derivatives of being replaced by amino groups. Experiments proved that these esters react with aromatic amines at their boiling point. The reaction takes place under the formation of the corresponding amino derivatives in the following manner:

$$B(OC_4H_9)_3 + 3\ RNH_2 \rightleftharpoons B(NHR)_3 + 3C_4H_9OH$$

$$R'B(OC_4H_9)_2 + 2\ RNH_2 \rightleftharpoons R'B(NHR)_2 + 2C_4H_9OH$$

$$R'_2BOC_4H_9 + RNH_2 \rightleftharpoons R'_2BNHR + C_4H_9OH$$

Herefrom it follows that these are reversible reactions. The transformation of the ester into the amine can only be achieved by eliminating the alcohol from the reactant. The alcoholysis

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Organoboron Compounds. XLV. Reaction of Butyl Esters of Boric Acid and Boronorganic Acids With Aromatic Amines

of the amino derivatives takes place much more rapidly than the substitution of the amino groups for the alkoxyl as exemplified by the reaction of phenyl di-(phenylamino)-boron $\left[(C_6H_5B(NHC_6H_5)_2\right]$. When the alcohol is separated from the reactant by distillation, the above-mentioned reactions take place only if amines are used that have a higher boiling point than the alcohol formed in the reaction. In the present paper the reactions of the isobutyl esters of boric, n-propyl, phenyl, and diphenyl boric acid as well as of the n-butyl esters of n-butyl, and di-n-butyl boric acid with aniline and p-toluidine are described. Hereby only those products were obtained in which all alkoxy groups were fully substituted, which could be explained by stage (I) and (II) of the reaction. The results obtained prove that the substitution rate of the aryl amino groups for the alkoxy groups in the esters of boric, phenyl boric, and diphenyl boric acid is inverse to the rate of hydrolysis of the same esters (Refs 7, 8). The following compounds were synthesized in this way: tri-(p-tolylamino)-boron, phenyl di-(phenylamino)-boron, phenyl di-(p-tolylamino)-boron, n-propyl

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di-(phenylamino)-boron, n-butyl di-(phenylamino)-boron, di-phenyl-(phenylamino)-boron, and di-n-butyl-(phenylamino)-boron. The reaction rate of aniline with the esters increases in the series of the esters of boric acid in accordance with the gradation scheme boric acid ester < ester of phenyl boric acid < ester of diphenyl boric acid. There are 2 figures, 1 table, and 12 references, 7 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: July 10, 1958

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5(3) SOV/79-29-9-68/76

AUTHORS: Mikhaylov, B. M., Shchegoleva, T. A.

TITLE: Organoboron Compounds. XLVI. Dialkyl Boric Acids and Their Derivatives

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 9, pp 3130-3135 (USSR)

ABSTRACT: Alkylborates may serve for the synthesis of symmetrical and unsymmetrical dialkyl borates. The butyl esters of di-n-butyl- and n-propyl-n-butyl boric acid were synthesized by reaction of n-butyl lithium or n-propyl lithium with the n-butyl ester of n-butyl boric acid (Ref 11). Based on this method n-butyl-ethyl-n-butyl borate and n-butyl-ethyl-n-propyl borate were obtained here according to the scheme:

$$RB(OC_4H_9)_2 + C_2H_5Li \longrightarrow C_2H_5RBOC_4H_9 + C_4H_9OLi,$$

where R = C_4H_9, n.-C_3H_7. The synthesis of dialkyl borates on the basis of alkyl borates can also be practiced with organo-magnesium compounds. Thus, a 45% yield of n-butyl-di-n.-propyl borate was obtained by reaction of n.-propyl magnesium bromide with n.-butyl-n.-propyl borate:

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$n.\text{-}C_3H_7B(OC_4H_9)_2 + n.\text{-}C_3H_7MgBr \longrightarrow (n.\text{-}C_3H_7)_2BOC_4H_9$. The dialkyl boric acids resulted from saponification of dialkyl borates. The stability of dialkyl borates to hydrolyzing agents is conditioned by the nature of the arrangement of esters(for examples see references 8, 10). In this regard, n.-butyl dialkyl borates are much more stable than glycol esters (Refs 12, 13). The reaction of n.-butyl-di-n.-butyl borate with a 10% caustic soda solution with subsequent acidification is shown by scheme 1. Butyl alcohol is also completely eliminated together with water in the concentration of a salt solution (I) gently heated and distilled in vacuum. The crystalline residue is a sodium salt of di-n.-butylborenium acid (II) in analytically pure state. The reaction process of the formation of salt (II) is explained by scheme (2). Di-n.-butyl boric acid (Scheme 5) results from acidification of salt (II) after an intermediate stage of acid (V). Di-n.-propyl boric acid and n.-propyl-n.-butyl boric acid are colorless liquids tending to pass over into the corresponding anhydrides when they are heated. There are 14 references,

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Organoboron Compounds. XLVI. Dialkyl Boric Acids and Their Derivatives

4 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: July 10, 1958

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SOV/20-126-3-32/69

5(2,3)
AUTHORS: Mikhaylov, B. M., Vaver, V. A., Bubnov, Yu. N.

TITLE: Organoboron Compounds (Bororganicheskiye soyedineniya). Reactions Between Boron Trialkyls and Compounds Containing Mobile Hydrogen (Reaktsii bortrialkilov s soyedineniyami, soderzhashchimi podvizhnyy vodorod)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 3, pp 575 - 578 (USSR)

ABSTRACT: The ability of aliphatic boron compounds to undergo the reactions mentioned in the subtitle is very little investigated (Refs 1-6). Triallyl boron possesses, however, an extraordinary sensitivity to the reagents mentioned in the subtitle. It reacts with water, alcohols and amines, even at room temperature. One or two allyl radicals are replaced by corresponding groups. For these reasons, the subject mentioned in the subtitle was of considerable interest. The influence of the nature of initial substances on the rupturing process of the boron-carbon compound could be established. The authors studied the reactions between tri-n-propyl-, tri-isopropyl-tri-n-butyl, tri-isobutyl- and tri-isoamyl-boron on one hand, and water, alcohol, phenol, amines and

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mercaptans on the other hand. It has been found that higher boron trialkyls react energetically with water at 160-170°. Dialkyl boric acids (I) are formed which are isolated in the distillation as acid anhydrides with yields of 65-71% (Table 1). The reaction is accompanied by the formation of olefine hydrocarbons and hydrogen as well as saturated hydrocarbons (see Scheme). The occurring relative hydrocarbon- and hydrogen quantities depend on the test conditions. Boron trialkyls react under the same conditions with aliphatic alcohols or with phenol. Thus, they form alkyl or phenyl ester of the dialkyl boric acids (II) with yields of 65-80%, as well as saturated and olefine hydrocarbons and hydrogen. These reactions, as well as those of the aliphatic and aromatic amines (III), finally those of the mercaptans (IV), proceed in stages: they run through a stage of complex compounds of boron trialkyls and oxygen-, nitrogen- and sulphur-addenda (V). These compounds (V)(1) undergo two kinds of transformations: a) the complexes decompose into saturated hydrocarbons and corresponding organoboron compounds (VI)(2). It seems here that a proton is removed from the heterogeneously bound atom, and the alkyl group is split

off as an anion from the boron atom. b) Olefine hydrocarbon and hydrogen are eliminated and formed (VI) according to scheme (3). This process is most distinctly marked at the interaction of the boron trialkyls with water, alcohols and amines. The transformation of complexes (V) according to scheme (3) is also possible with the formation of dialkyl boranes (VII) which then separate a hydrogen molecule. The above reactions are simple and easy methods of producing the mentioned compounds. There are 1 table and 10 references, 2 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

PRESENTED: February 9, 1959, by B. A. Kazanskiy, Academician

SUBMITTED: February 9, 1959

SOV/20-127-3-25/71

5(2,3)

AUTHORS: Mikhaylov, B. M., Bubnov, Yu. N.

TITLE: Dialkylthioboric Acids and Borocyandialkyls

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 3, pp 571 - 574 (USSR)

ABSTRACT: The esters of the acids mentioned in the title which the authors developed by the influence of sulphur (Ref 1) or n-butyl-mercaptan (Ref 2) on borotrialkyls, are very reactive. Their reactivity exceeds that of their oxygen analogues. In the course of further investigations it was proved that thioesters not only react with amines, but also with H_2S and HCN.

If thioester, heated to 140-180° permeates H_2S, the acids mentioned in the title and mercaptan will develop and can be distilled according to their development. This is the way the authors produced di-n-butyl-, di-n-propyl- and di-isoamyl-thioboric acid from the n-butyl esters of the mentioned acids. These are the first representatives of this type of organic boric compounds. The properties and further transformations of thio acids are described. N-butyl-esters of the acids

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mentioned in the title, react with HCN at low temperature or with slight heating, and produce the alkyls (III, mentioned in the title. They are nitriles of unknown dialkyl-boric-carboxylic acids. If the ethereal solutions of n-butylester of Di-n-butyl-boric acid is mixed with HCN, heating occurs. A jellied precipitation develops which at first is colorless. This indicates the formation of complex compounds (II) in the first stage of the reaction. They soon change again. From the cryoscopic molecular weight, determined by means of benzene, one can see that they are associated up to a certain extent. A description is given of the physical properties of the above mentioned substances produced in this connection. Borocyandialkyls react with alcohols, if heated. At the same time esters of dialkylthioboric acids and HCN develop. Crystalline complex compounds (IV), inconstant if exposed to air, develop under the influence of amines on the mentioned radicals. Finally the authors mention the known cyanogen derivatives of the quadrivalent negative boron (Ref 4) and denote that the borocyandialkyls, as well as their complex compounds, together with amines, are the first representatives of the complex organic compounds of trivalent boron, containing a cyanogen

group. There are 5 references, 3 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

PRESENTED: April 3, 1959, by B. A. Kazanskiy, Academician

SUBMITTED: March 31, 1959

SOV/20-127-5-25/58

5(2,3)

AUTHORS: Mikhaylov, B. M., Kozminskaya, T. K., Fedotov, N. S., Dorokhov, V. A.

TITLE: Esters of Organothioboric Acids and Some of Their Transformations

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 5, pp 1027-1029 (USSR)

ABSTRACT: Since the esters of dialkyl thioboric acids (Refs 1, 2) proved to be very reactive compounds which may be used for the synthesis of various organoboric compounds the authors were interested in the production of the acids mentioned in the title and in their behaviour. The known aliphatic monosubstituted and the aromatic substituted esters of the thioboric acids are enumerated (Refs 3-5) and their production methods are mentioned. The authors found that the n-butyl esters of the alkyl thioboric acids (Ref 1) are produced in good yields in the boiling of the alkyl boron dichlorides and -dibromides with n-butyl mercaptan (see Scheme). By the same method n-butyl ester of the phenyl thioboric acid (II) was produced. Diphenyl boron chloride and di-α-naphthyl-boron chloride react in similar way with n-butyl mercaptan and form n-butyl esters of diphenyl thioboric acid (III. Ar = C_6H_5) and of di-α-naphthyl thioboric acid

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(III. Ar = α-$C_{10}H_7$). All esters produced are highly reactive. This permits their transformation into other organoboric compounds. By the action of ethylene diamine the mentioned esters are smoothly transformed into cyclic compounds, under the separation of n-butyl-mercaptan i.e. into 2-alkyl-2-boron-1,3-diazolidine (IV). In the action of ammonia on the esters of alkyl- and aryl thioboric acids at low temperatures the two latter were transformed into the corresponding boron trialkyl- and boron triaryl borazoles (V). The reaction between the ester and the phenyl thioboric acid and diethyl amine takes place in one direction under the formation of phenyl-di(diethyl amino)boron with a yield of 80%, whereas the amino compound (VI) is produced from the phenyl boron dichloride only in a 14% yield (Ref 8). Under the action of n-butyl ester of diphenyl thioboric acid is transformed into diphenyl butyl amino boron (VII) in the action of n-butyl amine in a 80% yield. The esters of

Esters of Organothioboric Acids and Some of Their Transformations

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diphenyl thioboric and di-α-naphthyl-thioboric acid react with ammonia at low temperatures. In this connection diphenyl amino boron (VIII. Ar = C_6H_5 see Scheme) are formed or di-α-naphthyl-amino-boron (VIII. Ar = α-$C_{10}H_7$). There are 9 references, 5 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

PRESENTED: April 20, 1959, by B. A. Kazanskiy, Academician

SUBMITTED: April 18, 1959

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81554
S/062/60/000/05/03/000
B004/B066

5.3700C

AUTHORS: Mikhaylov, B. M., Vaver, V. A.

TITLE: Organoboron Compounds. 56. Synthesis of Trialkylborons From Metaborates and Their Conversion Into Dialkyl Boric Acid Esters

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 5, pp. 852-856

TEXT: A thorough investigation of the reaction of trimeric metaborate with Grignard reagent in vacuo at low temperature and in the presence of water excess revealed that the formation of dialkyl boric acid esters takes place via the intermediate stage of trialkylborons. At 9 - 9.5 M Grignard reagent 70 - 80% trialkylboron was obtained, i.e.: triisopropyl-boron, tri-n-butylboron, and triisoamylboron. To check the assumption that the esters of the dialkyl boric acids are formed only by reaction of trialkylborons with alcohol, the afore-mentioned trialkylborons were allowed to react with cyclohexyl-, sec.-octyl- and isoamyl alcohol, and the following compounds were obtained: sec.-octyl ester of the di-iso

Organoboron Compounds. 56. Synthesis of Trialkylborons From Metaborates and Their Conversion Into Dialkyl Boric Acid Esters

propyl boric acid, cyclohexyl ester of the diisopropyl boric acid, isoamyl ester of the di-n-butyl boric acid, phenyl ester of the diisoamyl boric acid. The data of these compounds are given in a table. The authors discuss the course of the reaction between trialkylborons and alcohols and give the following reaction equations:

$R_3B + R'OH \longrightarrow R_3B{\leftarrow}O\begin{smallmatrix}H\\R'\end{smallmatrix}$ (Formation of a complex compound (I)). This compound decomposes according to equation (1): $R_3B{\leftarrow}O\begin{smallmatrix}H\\R'\end{smallmatrix} \longrightarrow R_2BOR' + RH$, or reacts according to equation (2) to form the complex (II):

$R_3B{\leftarrow}O\begin{smallmatrix}H\\R'\end{smallmatrix} \longrightarrow R_2BH{\leftarrow}O\begin{smallmatrix}H\\R'\end{smallmatrix}$ + olefin. The complex (II) decomposes according to equation (3): $R_2BH{\leftarrow}O\begin{smallmatrix}b\\R'\end{smallmatrix} \longrightarrow R_2BOR' + H_2$. The rate of the reactions (1) and (2) - (3) depends on the nature of the trialkylboron and alcohol applied. In the case of sec.-octyl alcohol and triisopropylboron the ratio of the two reaction rates is 1 : 2.5. The reaction with cyclohexanol takes place according to equations (2) and (3), whereas in the reaction of tri-n-butylboron with isoamyl alcohol both reactions pro-

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Organoboron Compounds. 56. Synthesis of Trialkyl-borons From Metaborates and Their Conversion Into Dialkyl Boric Acid Esters

with equal rate. As may be seen from the preparation of the phenyl ester (at 170 - 180°C), the reaction is possible also with phenols. There are 1 table and 8 references: 4 Soviet, 2 German, and 2 American.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: November 3, 1958

MIKHAYLOV, B.M.; PAVAROV, L.S.

Cyclization of ethoxyfarnesenic acid. Izv.AN SSSR Otd.khim. nauk no.5:935-936 My '60. (MIRA 13:6)

1. Institut organicheskoy khimii im. N.D. Zelinskogo Akademii nauk SSSR.
(Farnesenic acid) (Cyclization)

MIKHAYLOV, B.M.; SAVEL'YEVA, I.S.

Structure of the bromide $C_{10}H_{11}Br$, formed when bromine reacts with 2-phenyl-2-butanol or 2-phenyl-2-butene. Izv.AN SSSR.Otd. khim.nauk. no.6:1049-1052 Jl '60. (MIRA 13:7)

1. Institut organicheskoy khimii imeni N.D.Zelinskogo Akademii nauk SSSR.
(Butene) (Butanol)

S/062/60/000/007/013/017/XX
B004/B064

AUTHORS: Mikhaylov, B. M., and Ter-Sarkisyan, G. S.

TITLE: Polyene Compounds. Communication 1. Asymmetrical 1,6-Diaryl-substituted Hexatrienes 1,3,5

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 7, pp. 1267 - 1271

TEXT: In a previous paper the authors have described a simple method of synthesizing 5-phenyl pentadien-2,4-al-1 from the diacetal of cinnamic acid and vinyl ethyl ether. Thus, this aldehyde became easily accessible to various syntheses, especially to the synthesis of asymmetrical 1,6-disubstituted hexatriene-1,3,5 derivatives. In the present paper, the authors report on the syntheses carried out with 5-phenyl pentadien-2,4-al-1: 1) 1,6-diphenyl hexatriene-1,3,5 (A) a) by means of the Grignard reagent obtained from magnesium and benzyl chloride. The reaction is carried out in absolute ether (yield: 26.5%); b) with benzyl sodium in toluene (yield: 31.5%);

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Polyene Compounds Communication 1' S/062/60/000/007/013/017/XX
Asymmetrical 1,6-Diaryl-substituted B004/B064
Hexatrienes-1,3,5

c) with phenyl acetic acid in acetanhydride in the presence of litharge and boiling in nitrogen atmosphere yield: 34.5% 2) 1-phenyl-6 (α-naphthyl)-hexatriene-1,3,5 (B) with α-naphthyl acetic acid in acetaldehyde and in the presence of litharge; yield: 20.4% Contrary to A, this compound luminesces strongly both in crystallized and dissolved state. 3) 1-phenyl-6-(9-phenanthryl)-hexatriene-1,3,5 (C) by means of the Grignard reagent from Mg and 9-chloro methyl phenanthrene in ether. This compound luminesces 4) 1-phenyl-5-hydroxy 6-(p-biphenyl)-hexadiene-1,3 (D) by means of the Grignard reagent from Mg and 4-phenyl benzyl chloride in absolute ether 5) 1 phenyl-6-(p-biphenyl)-hexatriene-1,3,5 (E) by boiling of D in glacial acetic acid 6) 1-phenyl-6-(2 pyridyl-hexatriene-1,3,5 (F) with α-picolyl-lithium in absolute ether. 7) 1-phenyl-5-hydroxy-6 (2 quinolyl) hexadiene-2,4 (G) with quinaldyl-lithium in ether 8) 1-phenyl-6-(2-quinolyl)-hexatriene-1,3,5 (H) by boiling of G in acetic acid. The introduction of heterocyclic substituents (E and G) leads to a weaker luminescence. In a later paper the authors will report on the optical properties of these compounds

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Polyene Compounds. Communication [illegible]
Asymmetrical [illegible],6-Diaryl-substituted
Hexatrienes-1,3,5

S/062/60/000/007/013/017/XX
B004/B064

There are 5 references: 3 Soviet, 1 US and 1 Swiss.

ASSOCIATION: Institut organicheskoy khimii im N D Zelinskogo
Akademii nauk SSSR
(Institute of Organic Chemistry imeni N D Zelinskiy
of the Academy of Sciences USSR)

SUBMITTED: December 27, 1958

Card 3/3

Mikhaylov, B.M.

5.3700(B)

82103
S/062/60/000/07/07/007
B015/B054

AUTHORS: Mikhaylov, B. M., Shchegoleva, T. A., Blokhina, A. N.

TITLE: Reaction of Tetra-n-butyl Mercapto Diborane with Unsaturated Compounds

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 7, pp. 1307-1309

TEXT: The olefin hydrocarbons (hexene-1, octene-1, styrene) react with tetra-n-butyl mercapto diborane at 70-80°C in the presence of pyridine under formation of the n-butyl esters of alkyl thioboric acids. The reaction between tetra-n-butyl mercapto diborane and propylene or isobutylene proceeds in a complicated way. On heating tetra-n-butyl mercapto diborane with propylene in the presence of pyridine in an autoclave at 70-80°C and 5-15 atm, the n-butyl ester of n-propyl thioboric acid as well as the n-butyl ester of di-n-propyl thioboric acid and tri-n-butyl thioborate are formed. Tetra-n-butyl mercapto diborane reacts with isobutylene in a similar way; a mixture consisting of the esters of isobutyl thioboric- and diisobutyl thioboric acid as well as tri-n-butyl

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Reaction of Tetra-n-butyl Mercapto Diborane With Unsaturated Compounds

82103
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BC15/B054

thioborate are formed. The formation of the esters of dialkyl thioboric acids and of thioborate is explained by the fact that tetra-n-butyl mercapto diborane symmetrizes to thioborate and di-n-butyl mercapto diborane, and the latter reacts with the olefins under formation of the corresponding esters of dialkyl thioboric acids. There are 3 Soviet references.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR
(Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: December 24, 1959

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S/062/60/000/008/017/033/XX
B013/B055

AUTHOR: Mikhaylov, B. M.

TITLE: Covalent Carbon Radii and the Question of Conjugation

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 8, pp. 1379-1386

TEXT: In the present paper the author deals with the concept of resonance and the role of carbon orbital hybridization in the shortening of interatomic distances, a question of great interest in theoretical organic chemistry. The considerable number of interatomic distances determined precisely up to the present enabled the present investigation. Exact measurements of interatomic distances were possible due to the development of microwave spectroscopy. A review of the published experimental data showed that the covalent carbon radii in the sp^2 and sp states are 0.73 and 0.69 A respectively. It was shown that hyperconjugation of the first order (σ, π conjugation) does not exist. The shortening of a single carbon-carbon bond adjacent to a multiple bond is not due to the electron shift assumed in the hyperconjugation mechanism (resonance), but to an

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orbital effect, i.e., a contraction of the covalent carbon radii due to an increase in bonding s orbitals. It was also found that in molecules with alternating multiple bonds a π-electron shift, and thus an equalization of bond lengths, does not take place. The mesomeric (conjugation) effect (static effect of π,π conjugation) postulated by the concept of resonance does not occur in this type of molecule. The contraction of single bonds in molecules with alternating multiple bonds is due to the orbital effect. All data given are taken from publications. Mention is made of M. F. Mamotenko, V. M. Tatevskiy, M. I. Batuyev. There are 1 figure, 2 tables, and 30 references: 5 Soviet, 17 US, 4 British, 2 Belgian, 1 Canadian, and 1 Danish.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: March 6, 1959

87120

S/062/60/000/009/02[illegible]
B023/B064

53700 2209, 1273, 1236

AUTHORS: Mikhaylov, B. M. and Fedotov, N. S.

TITLE: Organoboron Compounds. Communication 56. The Effect of Amines and Ammonia Upon Diaryl Boron Chlorides

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khim. [illegible] nauk, 1960, No. 9, pp. 1590-1594

TEXT: The authors investigated organoboron compounds and the effect of amines and ammonia upon diaryl boron chlorides. Aniline, the primary aromatic amine, reacts with diphenyl boron chloride in the same manner as secondary alophatic amines, and forms diphenyl phenyl amine boron at room temperature. The aromatic radical bound to boron exerts also a strong influence upon the reactivity of diaryl boron chlorides. Di-α-naphthyl boron chloride was found to be converted into corresponding N-substituted derivatives of di-α-naphthyl amine boron both under the action of primary aliphatic and aromatic amines, and secondary aliphatic amines at room temperature. Thus, the following compounds were obtained: di-α naphthyl methyl amine boron, di-α-naphthyl isobutyl amine boron, di-α naphthyl

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87120

Organoboron Compounds. Communication [illegible] The Effect of Amines and Ammonia Upon Diaryl Boron Chlorides

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B023/B064

phenyl amine boron, and di-α-naphthyl diethyl amine boron. The behavior of diphenyl boron chloride and di-α-naphthyl boron chloride toward ammonia differs completely. When bubbling ammonia at low temperature through a benzene solution of di-α-naphthyl boron chloride, di-α-naphthyl amine boron forms readily. Diphenyl boron chloride forms a stable complex with ammonia (Ref. 2). A complete analysis showed that it is the diammoniate of diphenyl boron chloride, which probably has a heteropolar structure. The ammonium salt of diphenyl borenium acid $[(C_6H_5)_2B(OH)_2]^-NH_4^+$ forms during the hydrolysis of this complex. N-substituted derivatives of diphenyl amine boron and of di-α-naphthyl amine boron exhibit a different stability to water. The stability depends both on the nature of the aromatic radicals bound to the boron atom and on the character of the radicals in the amine group. Diphenyl phenyl amine boron and di α-naphthyl phenyl amine boron are easily hydrolyzed by atmospheric humidity, while di-α naphthyl diethyl amine boron does not even change when heated with water at 100 C for 1 h. Di-α-naphthyl amine boron, di-α-naphthyl methyl amine boron, and di α-naphthyl isobutyl amine boron do not change under the action of water at

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Organoboron Compounds. Communication 58. The Effect of Amines and Ammonia Upon Diaryl Boron Chlorides

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room temperature for one hour; they are, however, hydrolized by water at 100°C under the formation of the respective amine and the di-α-naphthyl boric acid. The latter decomposes into naphthalene and α-naphthyl boric acid. The authors think that the compounds are more stable to water than hexamethyl borazole which is hydrolized with water at room temperature. Thus, the authors conclude that the relative stability of borazole and its derivatives to hydrolizing agents is not only characteristic of cyclic compounds with boron - nitrogen bonds, but also of some nitrogen compounds of boron with an open chain. There are 4 references: 4 Soviet and 1 German.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akadem. nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: March 31, 1960

Card 3/3

S/062/60/000/009/[illegible]
B023/B064

AUTHORS: Mikhaylov, B. M. and Kiselev, V. G.

TITLE: Radiation-chemical Transformations of Organic Substances. Communication 4. Oxidation of Ethylene by Oxygen Under the Action of Fast Moving Electrons

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 9, pp. 1619-1628

TEXT: The authors studied the oxidation of ethylene by oxygen in the gaseous phase under the action of a beam of fast moving electrons. The following problems were clarified: effect of the radiation time, ratio of the initial gases, temperature and material of the reaction vessel. Experiments on the effect of the total dose upon the oxidation process were carried out with ethylene - oxygen mixtures. The ratio was 1 : 1. Further conditions: room temperature, initial pressure equal to the atmospheric pressure, the vessel - an aluminum chamber. The time of radiation was between 5 and 45 minutes, the radiation doses were $0.2 \cdot 10^{23}$ - $1.7 \cdot 10^{23}$ ev. Figs. 1-4 list the experimental results. It is

Radiation-chemical Transformations of Organic Substances. Communication 4. Oxidation of Ethylene by Oxygen Under the Action of Fast Moving Electrons

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shown that ethylene reacts quicker than oxygen at the mentioned doses The difference increases at a reduction of the total dose This phenomenon may be explained by the fact that in the initial period of the reaction, the acetylene and carbon monoxide yields increase due to the catalytic effect of the chamber walls. Glycolaldehyde, formic acid, carbon monoxide, acetylene, and organic peroxides (hydrogen peroxide in a very low yield) are the chief products of oxidation. The formaldehyde yield is 0.15 molecules/100 ev. The dependence of the oxidation process on the interrelation of the initial gases was investigated in the same chamber and under the same conditions. Time of exposure: 15 minutes, dose: $0.55 \cdot 10^{23}$ ev. Figs 5-8 show that the reaction rate of ethylene with oxygen strongly depends on the interrelation of the gases in the initial mixture. This dependence is greater in the case of ethylene The experimental results showed that the reduction of the ethylene content in the initial mixture leads to an almost complete oxidation of ethylene On the other hand an increase of the ethylene content increases the conversion of oxygen. An inverse dependence exists in the radiation-chemical

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Radiation-chemical Transformations of Organic Substances. Communication 4. Oxidation of Ethylene by Oxygen Under the Action of Fast Moving Electrons

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yields. The following data show that at small concentrations, formic acid and carbon monoxide are the chief reaction products. To study the effect of the walls of the reaction vessels upon the ethylene oxidation under the action of fast moving electrons, experiments were carried out in glass-, steel-, and brass chambers. Table 1 gives the experimental results. It can be seen herefrom that the ethylene oxidation in glass-, steel-, and aluminum chambers takes approximately the same course. A considerable decrease of the peroxide and glycolaldehyde yield and an increase of the yield in higher acids, carbon monoxide, formaldehyde, and butylene was noticed in the brass chamber. Brass acts upon the primary oxidation products and changes the direction of the secondary reactions. The temperature effect upon the process of ethylene oxidation was studied in an aluminum chamber on mixtures 1:1 in the temperature range of -40 - +80°, in a glass chamber the temperature range was -40 - +20°, at an exposure time of 15 minutes. Tables 2 and 3 give the results of these investigations. In general, the dependence of the ethylene oxidation under the action of fast moving electrons on temperature is not great. Finally, the

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Radiation-chemical Transformations of Organic Substances. Communication 4. Oxidation of Ethylene by Oxygen Under the Action of Fast Moving Electrons

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B023/B064

authors suggest a reaction mechanism which bases on the formation and further conversions of ethylene peroxide (see Scheme). The authors thank V. S. Bogdanov for his assistance in the research work. There are 8 figures, 3 tables, and 14 references: 5 Soviet, 5 US, 1 Czechoslovakian, 2 British, and 1 German.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: March 2, 1959

$$C_2H_4 \rightsquigarrow C_2H_4^+$$

$$C_2H_4^+ \xrightarrow{O_2} C_2H_4O_3$$

$$C_2H_4O_3 \longrightarrow HOCH_2CHO$$

$$C_2H_4O_3 \xrightarrow{O_2} 2HCOOH$$

$$C_2H_4O_3 \xrightarrow{C_2H_4} 2CH_3CHO$$

$$C_2H_4^+ + O_2 \longrightarrow 2CO + 2H_2$$

$$C_2H_4^+ + 2O_2 \longrightarrow 2CO + 2H_2O$$

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84859

S/062/60/000/010/013/018
B015/B064

11.1250

AUTHORS: Mikhaylov, B. M. and Bubnov, Yu. N.

TITLE: Catalytic Effect of Mercaptanes Upon the Conversion of Boron Trialkyls Under the Action of Ammonia, Amines, and Alcohols

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 10, pp. 1872 - 1873

TEXT: The smooth course of reaction between thioesters and ammonia allows to synthesize any dialkyl (amino) boron compounds (R_2BNH_2) from boron trialkyls, with mercaptane being used in quantities that cause catalytic effects. On introducing ammonia into normal boron tributyl or triisoamyl boron to which approximately 1/25 equivalent of normal butyl mercaptane had been added, normal dibutyl (amino) boron and diisoamyl (amino) boron were obtained in yields of 70-75%:

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Catalytic Effect of Mercaptanes Upon the Conversion of Boron Trialkyls Under the Action of Ammonia, Amines, and Alcohols

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$R_3B + R'SH \longrightarrow R_2BSR' + RH$ ($R = n\text{-}C_4H_9$, $i\text{-}C_5H_{11}$, $R' = n\text{-}C_4H_9$)

$R_2BNH_2 + R'SH \longleftarrow B_2BSR' \cdot NH_3$ The thioester formed by the first reaction regenerates mercaptane when reacting with ammonia; subsequently mercaptane reacts with boron trialkyl, and this process is repeated until boron trialkyl is entirely consumed. Thus, it is also possible to synthesize N-substituted dialkyl (amino) boron compounds and esters of dialkyl boric acids. By adding diethyl amine to n-tripropyl boron (with n-propyl mercaptane), n-dipropyl (diethyl amino) boron is obtained in a yield of 92%:

$$(n\text{-}C_3H_7)_3B + (C_2H_5)_2NH_2 \xrightarrow{n\text{-}C_3H_7SH} (n\text{-}C_3H_7)_2BN(C_2H_5)_2 + C_3H_8$$

The authors of the present paper state that in the synthesis of n-dibutyl (amino) boron carried out by Wiberg et al. (Ref.3), Booth and Kraus (Ref.4), as well as Evers et al. (Ref.5), not this substance is concerned, since the properties of n-dibutyl (amino) boron synthesized

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Catalytic Effect of Mercaptanes Upon the Conversion of Boron Trialkyls Under the Action of Ammonia, Amines, and Alcohols

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by the authors were other than those given by the afore-mentioned researchers. The difficultly accessible methyl esters R_2BOCH_3 were obtained by the reaction

$$(n\text{-}C_3H_7)_3B + CH_3OH \xrightarrow{n\text{-}C_3H_7SH} (n\text{-}C_3H_7)_2BOCH_3 + C_3H_8$$

By heating the mixture of n-dipropyl (amino) boron with dimethyl amine, it was possible to synthesize n-dipropyl (diethyl amino) boron. The individual syntheses are described. There are 6 references: 3 Soviet, 2 US, and 1 German

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: March 1, 1960

Card 3/3

84861

S/062/60/000/010/015/018
B015/B064

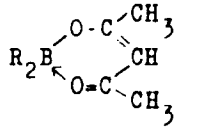
5 3700 2209, 1282, 1312

AUTHORS: Mikhaylov, B. M. and Bubnov, Yu. N.

TITLE: Chelate Acetyl Acetonates of Dialkyl Boric Acids

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 10, pp. 1883 - 1885

TEXT: In continuation of previous papers, the present article deals with the conversion of n-tripropyl- and tributyl boron, of the n-butyl ester of n-dibutyl thioboric acid, and of the methyl ester of n-dipropyl boric acid under the action of acetyl acetone. Three methods of synthesizing dialkyl boric acid acetyl acetonates (II) are described.



(II)

(R = n-C_3H_7, n-C_4H_9)

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84861

Chelate Acetyl Acetonates of Dialkyl Boric Acids

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B015/B064

After a short period of induction (apparently necessary to enolize acetyl acetone and to form borenium acid), a vigorous exothermic reaction sets in, in the first stage of which the anion of borenium acid splits off the radical R^- in the form of an anion which, together with a proton, forms a saturated hydrocarbon and is converted into acetonate (II). The acetyl acetonate of n-dibutyl boric acid was also obtained by heating the n-butyl ester of n-dibutyl thioboric acid and acetyl acetone. In the third method of synthesis, an esterification was carried out by heating the mixture of the methyl ester of n-dipropyl boric acid and acetyl acetone; thus, the acetyl acetonate of n-dipropyl boric acid was obtained. The resulting acetyl acetonates, golden-green, easily mobile liquids, were stable in dry air. The spectrum of the acetyl acetonate of n-dipropyl boric acid dissolved in CCl_4 is given in Fig. 1 and shows the bands of the C=C double bond and the complexly bound carbonyl group of the chelate β-dicarbonyl compounds. The spectra were taken by B. V. Lopatin on an ИКС-14 (IKS-14) spectrophotometer. There are 1 figure and 11 references. 5 Soviet, 2 German, and 4 British

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84861

Chelate Acetyl Acetonates of Dialkyl Boric Acids

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B015/B064

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: March 11, 1960

Card 3/3

86718
S/062/60/000/010/029/031/XX
B004/B060

,406 2209, 1153, 1820

...TORS: Mikhaylov, B. M. and Ter-Sarkisyan, G. S.

...LE: Synthesis of Mercaptals

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 10, pp. 1886-1887

TEXT: The recently much investigated reaction of aldehyde acetals with vinyl ethers meets with difficulties in some cases, because of the complicated character of synthesis of corresponding acetals. In the study under consideration the authors intended to simplify their task by using easily obtainable mercaptals, $RCH(SC_2H_5)_2$, instead of acetals. The following reaction is described: A mixture of ethyl mercaptan with $ZnCl_2$ and Na_2SO_4 is cooled down to -2°C, and aldehyde is added dropwise. The temperature must not exceed 0°C. After being allowed to stand in a refrigerator for ... h, the mixture is poured into ice water, the separating oil is extracted with ether, washed with 10% lye, and subsequently with water, dried over Na_2SO_4, and distilled in vacuum. Under these mild conditions, diethyl

Synthesis of Mercaptals

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B004/B060

mercaptals of cinnamaldehyde, 5-phenyl pentadien—2,4-al, citral, β-cyclo-citral, benzaldehyde, and furfurole were obtained in good yields (55.1-77.5%). A report is to follow concerning the condensation of these mercaptals with α,β-unsaturated ethers. L. S. Povarov is mentioned. There are 1 table and 10 references: 5 Soviet, 2 US, 1 Japanese, and 2 Swiss.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR
(Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: March 21, 1960

Card 2/2

3832 2209, 1234, 1274

S/062/60/000/010/030/031/XX
B004/B060

ORS: Mikhaylov, B. M. and Ter-Sarkisyan, G. S.

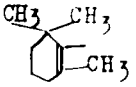
T: Condensation of Mercaptals With Vinyl Ethyl Ether

ERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 10, pp. 1888-1891

TEXT: In a previous paper (Ref. 2), the authors synthesized diethyl mercaptals of benzaldehyde, cinnamaldehyde, and β-cyclocitral. The article under consideration deals with the condensation of these compounds with vinyl ethyl ether. The reaction took place with mercaptal in the presence of BF_3 etherate or $ZnCl_2$ solution in ethyl acetate as a catalyst, addition by drops of vinyl ether without allowing temperature to rise, mixing with ether, and distillation of the ether extract in vacuum. The following scheme is given:

$RCH(SC_2H_5)_2 + CH_2 = CHOC_2H_5 \rightarrow RCH(SC_2H_5)CH_2CH(OC_2H_5)(SC_2H_5)$; R =  (I);

 -CH=CH-

Card 1/2 (II);  (III).

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Condensation of Mercaptals With Vinyl Ethyl Ether S/062/60/000/010/030/031 XX
B004/B060

The presence of the mercaptal group was proved by a sublimate (Ref. 5). Boiling with glacial acetic acid effects the conversion of synthesized compounds into unsaturated aldehydes. Cinnamaldehyde was obtained from 1-ethoxy-1,3-di-(ethyl mercapto)-3-phenyl propane (I), while 5-phenyl pentadien-2,4-al was obtained from 1-ethoxy-1,3-di-(ethyl mercapto)-5-phenyl pentene-4 (II). Saponification of (I) in the presence of 2,4-dinitro phenyl hydrazone (2,4 DNPH) gave 2,4-DNPH of 3-phenyl-3-ethyl mercapto propanal, which, on boiling with alcoholic HCl, was converted into 2,4-DNPH of cinnamaldehyde. The ethyl mercapto group, not the ethoxy group, is separated on further reaction of (I) with vinyl ethyl ether to form 1,3-diethoxy-1,5-di-(ethyl mercapto)-5-phenyl pentane. The structure of this compound was proved a) by reaction with sublimate (proof of the mercapto group); b) reaction with 2,4-DNPH: formation of 2,4-DNPH of 5-phenyl-5-ethyl mercapto penten-2-al, which was converted into 2,4-DNPH of 5-phenyl pentadien-2,4-al. There are 1 table and 7 references: 5 Soviet, 1 US, and 1 French.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: March 23, 1960

Card 2/2

MIKHAYLOV, B.M.; POVAROV, L.S.

Reactions of 1,3-dioxolanes with α,β-unsaturated ethers. Izv. AN SSSR Otd. khim. nauk no.10:1903-1904 O '60. (MIRA 13:10)

1. Institut organicheskoy khimii im. N.D. Zelinskogo Akademii nauk SSSR.

(Dioxolane)

MIKHAYLOV, B.M.; TUTORSKAYA, F.B.

Action of ethyl mercaptan on trillylborine. Izv. AN SSSR.Otd. khim. nauk no.11:2068 N '60. (MIRA 13:11)

1. Institut organicheskoy khimii im.N.D.Zelinskogo AN SSSR.
(Borine) (Ethanethiol)

S/062/60/000/012/017/024
B013/B054

AUTHORS: Mikhaylov, B. M. and Kozminskaya, T. K.

TITLE: Synthesis of B Trialkyl Borazoles From Alkyl Thioboric Esters

PERIODICAL: Izvestiya Akademii nauk SSSR Otdeleniye khimicheskikh nauk, 1960, No. 12, pp. 2247-2248

TEXT: The authors briefly report on a study of the reaction of n-butyl esters of alkyl thioboric acids with ammonia. The reaction proceeds at room temperature to give B-trialkyl borazoles in 80-86% yields. In the first reaction stage, aminothioester is formed which later on presumably condenses to borazole. The used n-butyl esters of n-propyl and n-butyl thioboric acid were synthesized by the action of n-butyl mercaptan to the corresponding alkyl boron dibromides (Ref. 1). Di-n-butyl ester of isopropyl thioboric acid was obtained for the first time, also by the action of n-butyl mercaptan on isopropyl boron dibromide. The latter was synthesized from isopropyl boric anhydride and boron tribromide by the method described in Ref. 2. B-trialkyl derivatives of borazole,

Card 1/2

Synthesis of B-Trialkyl Borazoles From Alkyl Thioboric Esters

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B013/B054

B-trimethyl borazole (Ref 3), and B-trialkyl borazole (Ref [illegible]), were formerly obtained by heating the corresponding boron trialkyls with [illegible] in an autoclave at 330°-450°C. All operations were carried out with organoboron compounds in a dry nitrogen medium. There are 4 references: 3 Soviet and 1 German.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: May 6, 1960

Card 2/2

S/074/60/029/008/001/001
B015/B054

AUTHOR: Mikhaylov, B. M.

TITLE: Borazol and Its Derivatives

PERIODICAL: Uspekhi khimii, 1960, Vol. 29, No. 8, pp. 972 - 992

TEXT: The present article gives a complete survey of publications on the chemistry of borazol with special consideration of periodicals of 1958 and 1959. All essential methods of synthesizing borazol and its derivatives are indicated and discussed. The article is divided into three sections. The first section deals with the methods of synthesizing the borazol ring: 1) Synthesis from diborane and its alkyl derivatives, 2) synthesis from boron trialkyls; 3) synthesis of borazol derivatives by means of boron trichloride; 4) synthesis with the use of ammonium salts and lithium boron hydride; 5) synthesis of borazol derivatives by means of N-substituted derivatives of amino boron dichloride; 6) synthesis of borazol derivatives from alkyl- or aryl boron dichlorides; 7) synthesis from N-substituted derivatives of alkyl- or aryl (diamino) boron; 8) synthesis from esters of aryl chloroboric acids; 9) synthesis

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Borazol and Its Derivatives

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from esters of organothioboric acids; 10) synthesis from tetra-alkyl-mercapto diboranes. The second section deals with transformations of functional borazol derivatives: 1) Synthesis of borazol and its derivatives from B-chloro derivatives of borazol; 2) synthesis of borazol derivatives from its N-alkyl- and N-aryl-substituted derivatives. The second section also indicates the most important properties of borazol and its derivatives which allow conclusions to be drawn as to the transition from one derivative to the other. At the end of the present paper, the chemical and physical properties of borazol and its derivatives are indicated (Tables 1-5), and discussed in the third section. The following names are mentioned in the paper: A. F. Zhigach, L. N. Kochneva, V. I. Mikheyeva, V. Yu. Markina, T. V. Kostroma, P. M. Aronovich, T. K. Kozminskaya, N. S. Fedotov, V. A. Dorokhov, T. A. Shcherbleva. There are 5 tables and 71 references: 13 Soviet, 13 German, 39 US, and 6 British.

ASSOCIATION: In-t organicheskoy khimii AN SSSR im. N.D. Zelinskogo (Institute of Organic Chemistry of the AS USSR imeni N. D. Zelinskiy)

Card 2/2

MIKHAYLOV, B.M.; TER-SARKISYAN, G.S.

Polyene compounds. Part 12: Condensation of 5-phenyl-2,4-pentadienal with arylacetic acids. Zhur.ob.khim. 30 no.8:2521-2524 Ag '60. (MIRA 13:8)

1. Institut organicheskoy khimii Akademii nauk SSSR.
(Acetic acid) (Pentadienal)